Orientational Ordering of C_<60> Adsorbed on the Cu(111)1x1 Surface Studied by the FI-STM

Sci. Rep. RITU A39 (1993) pp. 51-55
No. 1, December 1993

Orientational Ordering of C_{60} Adsorbed on the Cu(111)1x1 Surface Studied by the FI-STM*

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(Received November 30, 1993)

The adsorption of C_{60} molecules on the Cu(111)1x1 surface has been investigated by field ion-scanning tunneling microscopy (FI-STM). At the initial stage adsorption, C_{60} molecules are mobile on the terrace at room temperature and segregate to the steps to form linear chains. With increasing coverage, two-dimensional islands form with a close-packed configuration. Upon monolayer adsorption, highly ordered Cu(111)-(4x4)-C_{60} overlayer forms. Bias voltage-dependent STM images of the individual C_{60} molecule show unique intramolecular structures. The adsorption geometry is determined by analyzing the STM images and the intramolecular structures are interpreted as the local density of the states of C_{60} interacting with the substrate.

KEYWORDS: C_{60}, fullerenes, STM, intramolecular structure, orientational ordering

1. INTRODUCTION

The recent discovery of C_{60} and other fullerenes[1] has initiated new research studies,[2] especially after the successful extraction and purification of fullerenes by Krätschmer et al.[3,4] and the discovery of superconductivity by Haddon et al.[5] in K_3C_{60} crystals. Scanning tunneling microscopy (STM)[6] has been used to investigate the surface and electronic structure of C_{60} films on various substrates, such as Au(111) and (110),[7-10] Au(100),[11] Ag(111),[12] HOPG(0001),[13] GaAs (110),[14] and Si(111)[15,16] and (100).[17] On the HOPG(0001)[13] and GaAs(110)[14] surfaces, C_{60} molecules were imaged by STM as spherical protrusions and the contrast within individual C_{60} molecule (intramolecular structure) was not observed. This is understandable when we consider the surface inertness of these surfaces and free rotation of C_{60} molecules in the bulk fcc crystal. Kuk et al. reported very interesting observation on C_{60} adsorption on the Au(100) surface, showing a squeezed electronic density of states because of a strong interaction between C_{60} molecules and the substrate.[11] However they did not observe intramolecular structure of C_{60} molecules and concluded that C_{60} molecules are still rotating on this surface. In contrast, Chen et al. studied C_{60} adsorption on an evaporated Au substrate by STM operated in air and reported several types of intramolecular structures,[9] which they interpreted as π-electrons localized on every other carbon atoms. Zhang et al. observed intramolecular structures of C_{60} molecules on the Au(110) surface imaged in 0.1M $HClO_4$ solution.[10] They pointed out several patterns of the intramolecular structure, such as (a) one central "dark" ring surrounded by six rings and (b) one central ring surrounded by five rings, but the interpretations of these observations were not reported. Altman and Colton showed high quality STM images of C_{60} molecules adsorbed on the Au(111) surface.[8] They observed stripe type intramolecular structures of the C_{60} molecules adsorbed on the step of the Au(111) surface and also those in a close-packed monolayer film. Altman and Colton observed six-fold filled state images and five-fold empty state images from the same area of the C_{60} monolayer film on the Au(111) surface.[12] They proposed to interpret these images in terms of the symmetry of the adsorption site for the case of filled state images and the symmetry of the molecular states for the case of empty state images.

We have applied FI-STM / STS (field ion-scanning tunneling microscopy / spectroscopy),[18] on the C_{60} adsorption on the Si(111)7x7 and Si(100)2x1 surfaces and observed stripe type intramolecular structures.[15,17] It is reasonable that the dangling bonds on the Si(111) and Si(100) surfaces form chemical bonds with C_{60} molecules and suppress or stop the free rotation of C_{60} molecules, thus permitting observation of the intramolecular structures. The STM images were compared with theoretical calculation[19] and the intramolecular structures in the filled states STM images were interpreted as a mapping of the local density of states of the HOMO band of C_{60} monolayer film.[20] In this paper, we report C_{60} adsorption on the Cu(111)1x1 surface[21] and discuss the orientational ordering of the C_{60} molecules on the surface determined by analyzing the intramolecular structures of C_{60} molecules.

2. EXPERIMENT

The FI-STM is a high-performance scanning tunneling microscope (STM) equipped with a room temperature field ion microscope (RT-FIM). Details of the apparatus have been reported elsewhere.[18] The cleaning procedure of the Cu(111) surface was a combination of Ar sputtering and annealing. High purity (99.95%) C_{60} powder[22] was placed in a small Ta dispenser, which was heated to approximately 370°C by resistive heating to evaporate C_{60} molecules onto the Cu(111) sample, 1 cm away from the dispenser. The base pressure was $3x10^{-11}$ Torr, and the pressure during the C_{60} adsorption was below $1x10^{-10}$ Torr. For the STM imaging, sample biases (V_S) between -3.5V and +3.5V were used, while the tunneling current I_t was kept constant at 20pA.

*IMR, Report No. 1950

3. RESULTS AND DISCUSSION

Figure 1a shows the initial stage adsorption of C_{60} molecules on the Cu(111)1x1 surface at room temperature. The C_{60} molecules are mobile on the terrace and segregate to the steps and fill up adsorption positions on the steps (Fig. 1a). As the coverage increases, C_{60} molecules start to form two dimensional (2D) islands growing from the step edges towards the upper terrace. Further increase in C_{60} coverage at room temperature leads to a monolayer film of C_{60} (Fig. 1b). As shown in Fig. 1b, the steps formed in the C_{60} monolayer replicate those in the original Cu(111) surface. In the center of Fig. 1b, we see the 2nd layer of C_{60}. The monolayer film grown at room temperature shows less ordering (compared with the annealed film, see below), and we can observe several domains existing on this surface.

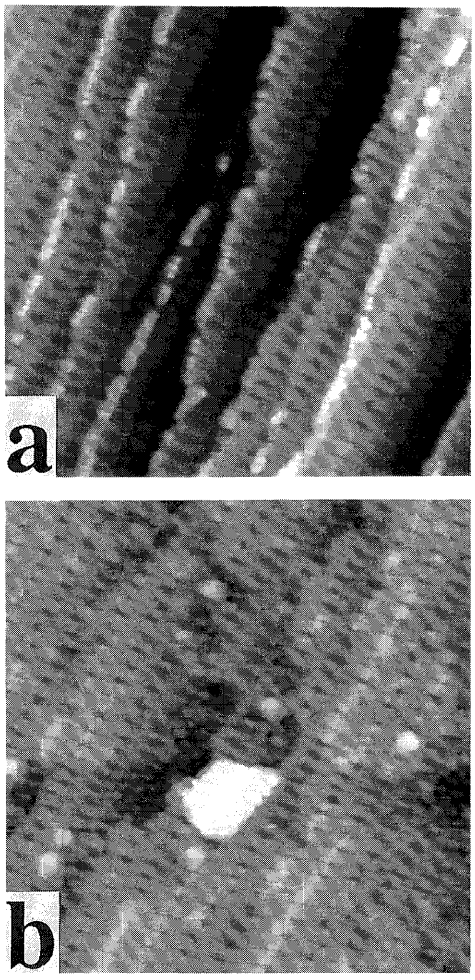

Fig. 1. Typical STM images of the Cu(111)1x1 surface covered with (a) 0.05ML (320Å x 320Å, V_s = -3.5V) and (b) monolayer film (320Å x 320Å, V_s = -2.0V) of C_{60} molecules deposited at room temperature.

Figure 2a and 2b show STM images of a C_{60} monolayer film formed after annealing at 290°C. The surface is highly ordered, except for point defects (white arrow around the center) and domain boundaries (black arrows). The steps again reflect the original Cu steps. An interesting observation is that the steps are lined up along the $< 0\bar{1}1 >$ direction, which is original Cu atomic row direction. This

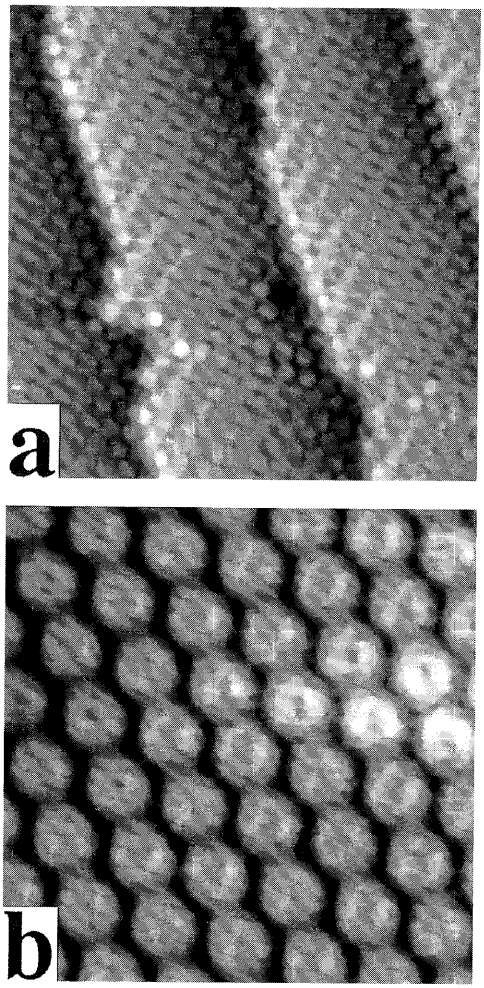

Fig. 2. High resolution STM images of the Cu(111)1x1 surface covered completely with a monolayer of C_{60} molecules prepared by annealing at 290°C. (a) Empty states image (230Å x 230Å, V_s = +2.0V), showing a three-lobe clover shape intramolecular structure of individual C_{60} molecules and (b) Filled states image (60Å x 60Å, V_s = -2.0V) with doughnut shape intramolecular structure.

indicates a large mass transport by annealing, forming a well ordered C_{60} monolayer film. The distance between nearest neighbor C_{60} molecules is 10.2Å, which is 4 times the nearest neighbor (nn) distance between Cu atoms on Cu(111). A recent study of C_{60} adsorption on the Cu(111), (110) and (100) surfaces using XPS and HREELS and other techniques[23] concluded that the single-domain epitaxy with a (4x4) overlayer and successive layer-by-layer growth can be achieved on the Cu(111) surface, which agrees well with the current observation by STM. Individual C_{60} molecules are imaged at the tunneling voltage of close to zero, which suggests that the gap states induced by electron charge transfer from the substrate to the overlayer enable us to image the molecule at the tunneling voltage within the HOMO-LUMO gap. The electron donation from the Cu substrate was also suggested by a photoemission study on the same Cu(111) surface.[23] The existence of gap states is evidence of the strong interaction between the Cu(111) substrate and the C_{60} molecules.

We note that individual C_{60} molecules appear in a three-lobe clover shape at V_S = +2.0V in Fig. 2a. When the surface is imaged at different bias voltages of V_S = -2.0V (Fig. 2b), each C_{60} molecules appears in a doughnut shape, almost round with a hole at the center. Similar to the case of C_{60} adsorption on the Si(100)2x1 surface,[17,20] the C_{60} molecules ratchet to a specific direction on terraces of the Cu(111) surface and intramolecular structures are observed.

In order to reveal the three-fold symmetry of a C_{60} molecule, one of the hexagonal rings of a C_{60} molecule should face down on the Cu(111) surface. If one of the pentagonal rings in the molecule faced the surface, the molecule should reveal a five-fold symmetry instead of the observed three-fold symmetry. If one of the carbon double bonds of a C_{60} molecule, interconnecting two hexagonal rings, faced the surface, the molecule would reveal a two-fold symmetry. There are two possibilities for the adsorption position, the atop site and the three-fold hollow site. Because we observe four domains and relative shift between domains is 1/3 of Cu-Cu distance (Fig. 1b, for instance), we conclude that the adsorption position should be the three-fold hollow site. Based on these analysis of the STM images, an adsorption orientation model of C_{60} molecule on the Cu(111) surface are derived as is shown in Fig. 3. In this model, three pentagonal rings surrounding one hexagonal ring are hatched. Note that three carbon atoms in the hexagonal ring facing the surface have almost perfect atop site on the surface Cu atoms (the size mismatch is only 4%).

Based on this adsorption model, the local density of states are calculated.[24] The fact that we can observe STM image at even around zero volt indicates that there is a large amount of charge transfer from Cu to C_{60}, at least more than the case of Si(111).[20] We are able to calculate the simulated images of intermolecular structures by evaluating the three dimensional map of the local electron density of states near the Fermi level. When we are observing the empty states, the 181 (LUMO band for neutral C_{60} crystal), 182 and 183 levels should contribute to the image. When we are observing the filled density of states, the 180, 179, 178, and 177 levels should contribute. Figures 4a and 4b show the calculated 3D map of local density of states which simulate the STM images in Figs. 2a and 2b, respectively. The agreement between experiment and simulation is evident. As a result, the clover leaves we observe at V_S = +2.0V correspond to three pentagonal rings surrounding a top hexagonal ring, exhibiting the t_{1u} symmetry, though it appears in a spherical shape for the rotating molecules on the defected area. The HOMO state image with h_u symmetry appears in a donut shape on the Cu(111).

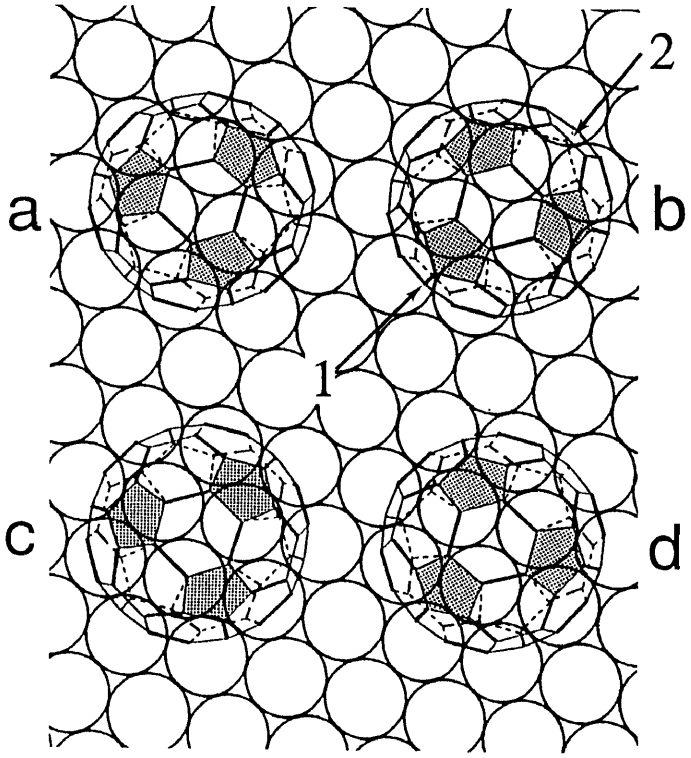

Fig. 3. Adsorption model for C_{60} on the Cu(111)1x1 surface. Three pentagonal rings of the C_{60} molecules are shaded for better viewing of the rotational freedom of each C_{60} molecule. The adsorption positions (a) and (b) are the fcc (hcp) sites and (c) and (d) are the hcp (fcc) sites. Arrows (1) and (2) indicate the directions, which have a double-bond and a pentagonal ring at the side of molecule, respectively.

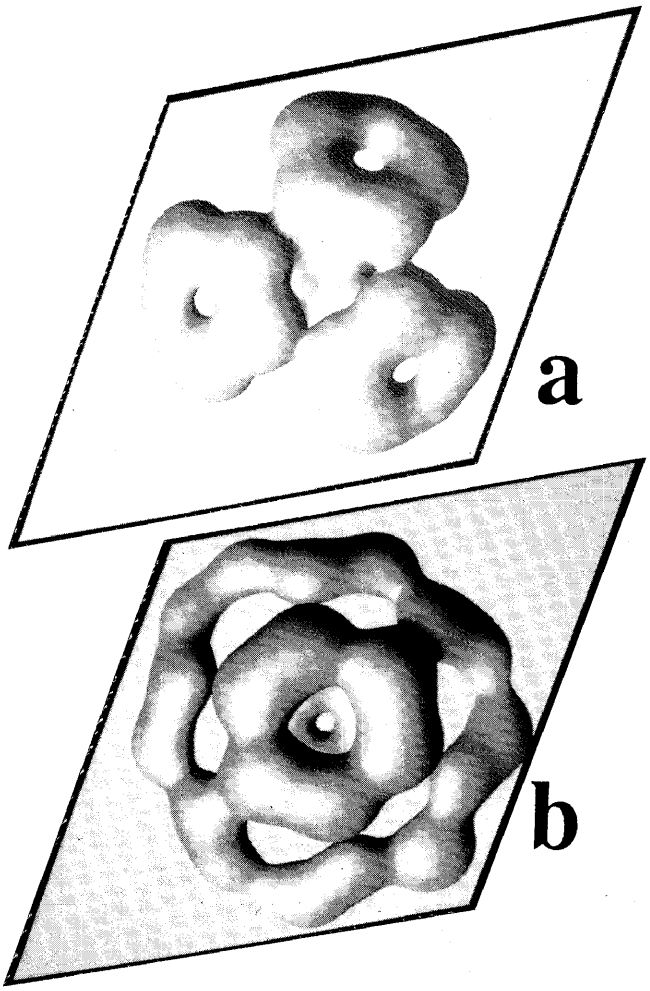

Fig. 4. Simulated STM images of a C_{60} molecule for V_S = (a) +2.0eV and (b) -2.0eV, obtained by calculating the local density of states near the Fermi level.

At room temperature, C_{60} molecules in the fcc lattice are orientationally disordered and below 255K, the system undergoes a first order phase transition to a simple cubic (sc) structure.[25] The phase transition is made by the orientational ordering of the C_{60} molecules, four of which in the fcc lattice become non-equivalent in the direction. This orientational ordering has been explained by the electrostatic interactions between electron-rich double bonds, interconnecting two hexagonal rings, and electron-poor pentagonal rings.[25]

In Fig. 2a, there are four terraces with the $<0\bar{1}1>$ directional step edges and each terrace is covered with hexagonal close packed C_{60} molecules. In the right three terraces, one of the three symmetric lobes representing the pentagonal rings are facing downward (in the $<01\bar{1}>$ direction), and in the leftmost terrace they point upward. It is evident that we observe orientational ordering of C_{60} molecules in a highly ordered monolayer film of C_{60} on the Cu(111) surface. It is interesting to note that the ordering can be maintained even beyond the steps. We can understand this if we consider that the step height of the Cu(111) surface (2.1Å) is less than 1/3 of the size of C_{60} molecules (7.1Å). The domain boundary seen in the center of Fig. 2a (indicated by black arrows) is also continuous beyond steps. If we examine the orientations of C_{60} molecules, we find that they have the orientations close to the orientations of C_{60} molecules in the sc bulk phase, namely one of the double bonds are almost facing to one of the pentagonal rings, as is shown in Fig. 3b by arrows (1) and(2). In Fig. 2a, we also notice that at a missing molecule defect site (indicated by a white arrow) or domain boundary (indicated by black arrows), C_{60} molecules appear to be rotating and are imaged as spheres. This indicates that orientational ordering shares an energetical contribution to ratcheting C_{60} molecules, although the main contribution may be the strong back bonding of atop site three carbon atoms in a C_{60} molecule with the Cu substrate atoms. The orientation of C_{60} molecules is aligned by the Cu(111) surface itself. If C_{60} molecules were in the bulk, where they have more freedom in orientation, they would rotate about 4° each, and form better alignment regarding the interaction between double bonds and pentagonal rings, which has been shown in the bulk sc phase.[25]

4. SUMMARY

By utilizing the FI-STM, we have examined C_{60} adsorption on the Cu(111)1x1 surface. At the initial stage, C_{60} molecules are mobile on the terrace and segregate to steps. After filling up the adsorption positions at the steps, they form 2D islands grown from steps to the upper terrace and then form 4x4 domains at the monolayer coverage. A large amount of charge transfer from the Cu substrate to C_{60} molecules is suggested from the STM imaging conditions. Because of the interaction between Cu surface atoms and C_{60} molecules and also because of the interaction associated with the orientational ordering of the C_{60} molecules, the rotation of the C_{60} molecules is inhibited. The bias-dependent intramolecular structures with three-fold symmetry are observed and interpreted as 3D mappings of the local charge density of states near the Fermi level.

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